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ALUMINUM-GOLD INTERACTION IN THIN LAYERS

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The reaction of contiguous films of aluminum and gold is studied at temperatures between 100-300°C with width ratios of δ_{Au}/δ_{Al} = 0.6-3.0. It was established that the character of the reaction and the composition of annealed films strongly depends on the temperature and time of exposure as well as the width ratio. The formation of intermetal compounds already occurs with noticeable speed at 100°. The diffusion coefficient and diffusion activation energy are evaluated by the curve of resistance change in various Au-Al width ratios. The order of magnitude of these coefficients indicates intercrystalline diffusion.

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In welding gold conductors and aluminum surfaces in silicon solid circuits as well as in heating a binary Au-Al film system, intercrystalline compounds are formed as a result of the reaction between the components [1-6]. Reference [3] concludes the presence of two different compounds in the contact area of the weld: a "black plague" developing at the point of contact between the gold conductor and the aluminized zone of the silicon, and a "purple-plague" developing at the point of contact between the aluminum wire and the gold pin. The authors of reference [3] suggest that silicon takes an active part in the formation of the black product while the purple compound is an intermetallic compound of aluminum and gold and corresponds to the formula $AuAl_2$. According to the data of [4] its specific resistance is 8 microhm·cm.

In reference [5], in which were studied massive Au-Al pairs of materials and the weld zone of gold beads with aluminum films on the surface of silicon, besides purple and black compounds, a silver area ("white plague") is found, which is assumed to be composed of a mixture of AuAl, Au_2Al, Au_5Al_2 (Au_8Al_3) phases.

* Numbers in the margin indicate pagination in the foreign text.

The interaction in Au-Al films in the range from room temperature to 164° was studied in reference [6], the authors of which conclude that prolonged annealing at this temperature leads to the formation of only two intercrystalline compounds, Au_2Al and $AuAl_2$.

As in the manufacture of microcircuits the deposition of several materials (for example, SiO) is combined with heating the substrate to 300°, it was of interest to study the interaction of a binary Au-Al film in a wider range of temperatures and thicknesses, which was the purpose of this work.

METHOD OF STUDY

Pyroceramic ST-50-1 was used as a substrate for all samples. Samples were coated in a UVN-2U unit at chamber pressure of $2 \cdot 10^{-5}$ mm Hg. To eliminate the development of an oxide film on the Au-Al boundary, a layer of gold was always deposited first. The gold was deposited at a rate of 25 Å/sec, aluminum at 50 Å/sec. To avoid interaction of the layers the substrate was not heated during deposition. The thickness ratio of the layers was varied in fabrication. To ensure identical conditions for producing samples with various thickness ratios, in depositing the gold a graduated layer was applied to the substrate through a mask. Over the graduated layer of gold an even layer of aluminum was deposited. After the substrate was cut, a batch of identical samples with a given thickness ratio was obtained. /530

It was established that air has no marked effect on reaction processes in the film, and subsequently samples were annealed in air. The annealing temperature varied between 100-300°, annealing time from several minutes to tens of hours.

The structure and composition of the films was examined roentgenographically after the annealings. Changes in their electrical resistance were recorded during annealing. The samples undergoing structural studies were divided according to the thickness ratio of the films $n = \delta_{Au}/\delta_{Al}$ into three groups: $n_1 \approx 0.6$, $n_2 \approx 1.2$ and $n_3 \approx 3.0$. To facilitate interpretation of roentgenograms, reference alloys were prepared with weight content of the components corresponding to the stoichiometric composition of compounds $AuAl_2$, AuAl, Au_2Al, Au_8Al_3, and Au_4Al.

The alloys, like the films, were made of high-purity materials: AV-000

aluminum and Z1 999.9 gold. Depending on composition, the beads of alloys ranged in color from yellow (rich in gold) to white (rich in aluminum) through gray and purple.

To raise resistance measured in the annealing process, a comb-shaped groove was cut on the film with a diamond blade, which made it possible to increase the length-width ratio of the measured film to 50. With an original specific surface resistance of the binary film on the order of 0.1 ohm/cm^2, the initial resistance of the sample was about 5 ohm.

EXPERIMENTAL RESULTS

Visual analysis of annealed samples showed the dependence of the intensity and direction of reactions on temperature and time of annealing and the thickness ratio of aluminum and gold. Table 1 gives the color of samples for three thickness ratios and a number of annealing temperatures.

TABLE 1. COLOR OF AU-AL SAMPLES AFTER ANNEALINGS (THICKNESS OF ALUMINUM FILM 1300 Å)

T, °C	Time of annealing, min.								
	20	60	180	20	60	180	20	60	180
	(800)			(1600)			(3800)		
100	N	N	N	N	N	N	N	N	N
150	N	N	P	N	P	P	N	DG	DG
200	N	N	P	P	P	P	DG	DG	DG
230	N	P	P	P	P	DG	DG	DG	DG
300	P	P	P	P	DG	DG	DG	DG	DG

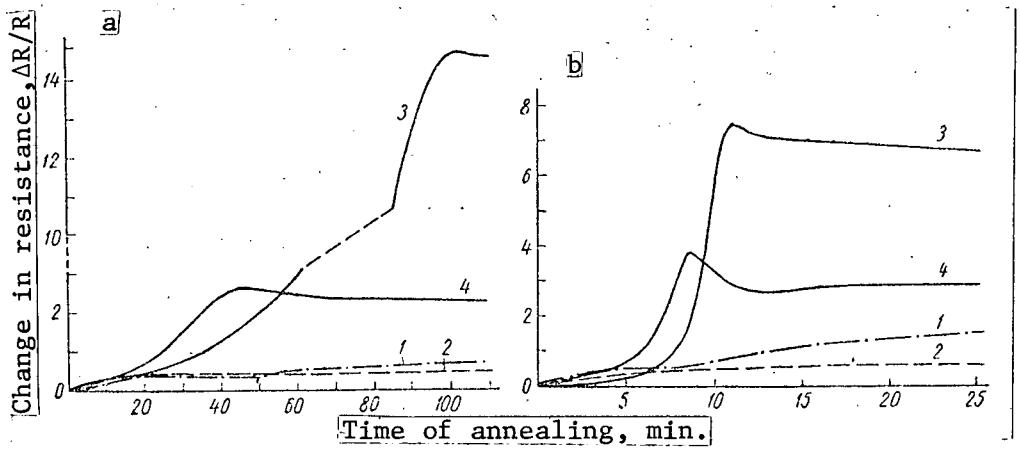
Note. N -- no visual changes in the condition of the surface of aluminum observed; P -- purple color ("purple plague"); DG -- dark gray color ("black plague"). In parentheses are shown the thickness of the gold films, Å.

Change in film color was accompanied by a sharp reduction in the reflective ability of the surface which changed from a mirror surface (typical of aluminum films) to dull, which was connected with the appearance of a more developed surface relief. Electron photomicrographs of the surface of individual samples show a noticeable large-aggregate structure after annealing above 200°.

/Röentgenostructural studies of reference alloys made it possible to identify positively four out of five compounds in the films indicated in the Al-Au diagram. It must be noted that on the powder diagrams of alloy 2, phases $AuAl_2$ and Au_2Al are detected, but no interference lines are found which could be attributed to the expected phase--the compound AuAl. It is possible that in cooling the conditions for its formation were not created.

According to roentgenostructural analysis data, the interaction between /531
gold and aluminum is already noticeable at 100°. First Au_2Al crystals are formed, later the $AuAl_2$ phase appears, then the amount of the first phase decreases until only $AuAl_2$ crystals with a purple color and excess gold remain in the sample. The process takes more than 150 hours to complete.

With a heating temperature of 150° or above, processes in different groups of films proceed differently. In films with a high aluminum content (n≈0.6), they follow the same sequence as at 100°, but at a greater rate. At 150° traces of Au_2Al disappear after 60 hours of heating, at 230°, after 60 min., and at 300° as little as 20 min. is sufficient for completion of the process. Only lines of $AuAl_2$ remain on roentgenograms of the films.



Change in resistance during isothermic annealing at 150° (a) and 230°C (b). Figures on curves correspond to numbers of batches given in Table 3.

In the group of samples with n≈1,2, in the initial minutes of annealing, crystals of Au_2Al and $AuAl_2$ are also formed first, but then the picture changes. The Au_2Al phase remains in the sample and even increases quantitatively, and the crystals of the "purple plague" undergo disintegration, ac-

companied by the appearance of a small number of crystals of a new unidentified phase. Eventually crystals of this phase appear in Au_2Al.

In gold rich films (n≈3.0), in no cases were "purple plague" crystals of $AuAl_2$ observed at 150° or above. First only crystals of Au_2Al appear, then Au_8Al_3 (Au_5Al_2) and slightly later Au_4Al. In proportion to the increased time of annealing, the amount of the latter phase increases and the first two are reduced. Finally, after 60 hours of heating at 150° or three hours of heating at 230°, only crystals of Au_4Al and gold are observed. At 300° the appearance of an unknown phase was noted in samples.

It follows from these data that in the interaction of Au-Al films the formation of structurally perfect crystals of compounds of $AuAl_2$, Au_2Al, Au_8Al_3 (Au_5Al_2) and Au_4Al is observed, as well as the formation of not less than two unknown phases. Interference lines of the Au_2Al phase undergo a slight change in passage from sample to sample with various prehistory. This agrees with the assumption of the authors of [7] that the formula of Au_2Al is only approximately accurate and boundaries of this phase extend in a certain range of concentrations. The other phases are more stable in structure and composition.

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TABLE 2. INTERPLANAR DISTANCES d (Å) FOR COMPOUND AU_2AL

d (data of [6])	Au_2Al				d (data of [6])	Au_2Al			
	Alloy		Films			Alloy		Films	
	d	I	d	I		d	I	d	I
4.48			(4.43)		1.61	1.61	M	1.61	M/W
	3.15	W	3.15	M	1.47	1.47	M	1.47	M/W
			(3.04)					1.44	Very W
2.79			2.79	Very W				1.38	Very W
			2.70	Very W				1.37	Very W
2.36	2.33	S	2.34	S	1.33	1.33	M	1.33	M/W
	2.22	S	2.22	S		1.31	M	1.31	M/W
	2.18	M	2.18	S/M	1.25	1.25	S	1.25	M
			2.12	Very W				1.20	Very W
2.08	2.07	W/M	2.07	W/M	1.18	1.18	W	1.18	W/M
			1.77	Very W				1.17	W
			1.68	Very W					

W -- weak; M-- medium; S -- strong.

TABLE 3. INTERPLANAR DISTANCES d (Å) OF AU_8AL_3

Au_8Al_3				Au_8Al_3			
Alloy		Films		Alloy		Films	
d	I	d	I	d	I	d	I
		3.71	Very W	1.585	M	1.587	M
3.37	Very W	3.37	W	1.546	W	1.551	W
		3.18	Very W			1.530	W
2.96	Very W	2.97	W			1.515	Very W
2.82	Very W	2.82	W	1.506	Very W	1.508	Very W
		2.61	Very W	1.484	Very W	1.484	W
		2.51	W			1.471	W
		2.45	W			1.457	Very W
		2.41	W			1.438	W
		2.35	Very W	1.425	W	1.427	S
2.31	W	2.32	W			1.410	Very W
2.26	S	2.26	S	1.398		1.398	Very W
2.22	S	2.22	Very S	1.389	Very W	1.390	W
2.09	W	2.10	W			1.375	W
1.925	W	1.928	M	1.357	M	1.364	M
1.850	W	1.855	W			1.347	Very W
1.775	Very W	1.780	W	1.331	Very W	1.331	W
		1.695	Very W	1.315	Very W	1.314	W
		1.649	W			1.306	Very W
		1.609	W	1.292	S	1.293	S
				1.284	S	1.285	S

W -- weak; M -- medium; S -- strong.

The literature lacks information on the interplanar distances and structure of Au_8Al_3 (Au_5Al_2) and the value of d is given only for several lines of Au_2Al [6]. It seems advisable to indicate the diffraction spectra of these phases. Tables 2 and 3 give the results of diffraction analysis, obtained from samples of reference alloys and film samples. The possibility is not excluded that several values of d have been missed because of overlapping of lines of various phases.

The change in electrical resistance during isothermal annealing at 150 and 230° is shown in the illustration. Three curves out of four in figure a have a maximum whose height and position along the time axis depend on the temperature of annealing and film thicknesses. The greatest increase of resistance (to 15 times) occurred in samples with a ratio of n≈2. The curve

for n≈0.8 has no maximum. At annealing temperature of 230° the shape of the curves is analogous, but more compressed in time (see figure b). /533

DISCUSSION OF RESULTS

Maximum increase of resistance in overlapping sections of Au-Al film is evidently determined by the ratio between concentrations of metallic components and intermetallic compounds. It is very probable that the 15-fold increase of resistance obtained on one of the tests is not the highest possible.

A comparison with data of roentgenostructural analysis indicates that the initial rise of the curves is connected with the formation of phase Au_2Al, as in the initial stage of the annealing process this phase is a common feature in all thickness ratios. The subsequent drop is evidently due to disintegration of Au_2Al and the formation of new phases, particularly $AuAl_2$, which has a lower specific resistance.

The shape of the curve with n = 1.61 supports this assumption: after a weak maximum, further rise of the curve continues. According to roentgenostructural analysis, with n = 1.2 the amount of the Au_2Al phase increases with time. The lack of maximum in the curve with n = 0.95 is probably due to a longer time of disintegration of the Au_2Al phase in a given thickness ratio. We shall evaluate possible values of the interdiffusion coefficient.

Assume that the activation energy of the formation of compounds is less than the activation energy of diffusion and that the time of attaining maxima on the curves corresponds to the time of discharge of the diffusion front to the surface of the film. Using the formula $x^2 = Dt$ (x -- the distance of the phase boundary from the initial bimetal boundary; D -- diffusion coefficient; t -- time), the diffusion coefficient and activation energy of diffusion Q can be estimated from the curves in Fig. a and b if x is taken as the greatest distance from the initial boundary to the surface of the film, i.e. the thickness of the gold film.

Table 4 gives calculated values of D and Q.

The literature contains no data on the activation energy of diffusion for solid Au-Al materials. According to [6], for bimetallic films the coefficient D at 84° is $1.01 \cdot 10^{-14}$ $cm^2/sec.$, and Q = 22.6 kcal/mole = 0.98 eV. In reference [8] activation energy of surface diffusion in films for copper through silver

TABLE 4. DIFFUSION CHARACTERISTICS OF AU-AL FILMS

Batch no.	δ_{Au}, μμ	δ_{Al}, μμ	T, °K	t_{max}, sec	D, cm^2/sec	Q, eV
1	0.29	0.18	423	1680	$5.0 \cdot 10^{-13}$	0.42
			503	270	$3.1 \cdot 10^{-12}$	
2	0.19	0.24	423	Not. det.	not det.	not det.
			503			
3	0.41	0.19	423	6000	$2.8 \cdot 10^{-13}$	0.49
			503	660	$2.5 \cdot 10^{-12}$	
4	0.36	0.12	423	3000	$4.3 \cdot 10^{-13}$	0.41
					$2.6 \cdot 10^{-12}$	

is 14 kcal/mole=0.61 eV. Coefficients of surface diffusion for this system /534
are 4-5 orders greater than those of volume diffusion. Similar activation energies were obtained for several bimetallic films in earlier publications, a review of which is given in [9].

The large difference in activation energies and diffusion coefficients between films and solid systems is due to the presence in films thermally precipitated in a vacuum of a large number of grain boundaries, which serve as channels for the diffusion of atoms along the surface of the section. At low temperatures, diffusion along the surface evidently dominates over volume. The difference between our results and data on the activation energy of diffusion for films is evidently due to the difference in film structure, depending on the thickness and conditions of precipitation.

CONCLUSIONS

Our observations showed that the purple color of samples is related exclusively to the formation of $AuAl_2$. When compounds Au_8Al_3 and Au_4Al which are richer in gold appear, the films acquire a dark gray color. The presence of silicon is not necessary for the formation of the black product, which contradicts the conclusions of reference [3].

Similar values of the diffusion coefficient, obtained by the curve of increased resistance in various thickness ratios of aluminum and gold, support the assumption that the rate of formation of intermetallic compounds is determined primarily by diffusion processes. The order of magnitude of these coefficients and the activation energy of diffusion indicate intracrystalline diffusion.

The interaction of gold and aluminum films, accompanied by the formation of intermetallic compounds, occurs even at 100°. With increased temperature the rate of the processes increases greatly and the character can change, depending on the thickness ratio of the films.

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